Benz(2-heteroaryl)cyanoximes and their Tl(I) complexes: new room temperature blue emitters†‡

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A series of five 2-heteroarylcyanoximes such as: α -oximino-(2-benzimidazolyl)acetonitrile (HBIHCO), α-oximino-(N-methy-l-2-benzimidazolyl)acetonitrile (HBIMCO), α-oximino-(2-benzoxazolyl)acetonitrile (HBOCO), α -oximino-(2-benzothiazolyl)acetonitrile (HBTCO) and α oximino-(2-quinolyl)acetonitrile (HQCO) and their monovalent thallium(I) complexes were synthesized and characterized using spectroscopic methods (¹H, ¹³C NMR, IR, UV-visible, mass-spectrometry) and X-ray analysis. The HBIMCO (as monohydrate) adopts planar trans-anti configuration in the solid state. The crystal structure of "HBOCO" revealed the presence of *nitroso* anion a, BOCO⁻, and protonated oxime cation b, H₂BOCO⁺, that form a H-bonded dimer in the unit cell. Both molecules adopt planar structures, but different configurations: *cis-anti* in the molecule *a*, and *trans-anti* for *b*. This is the first reported case of a zwitterionic pair in oximes and the coexistence of the two geometrical cis/trans isomers in the same crystal. All 2-heteroarylcyanoximes form yellow anions upon deprotonation, which exhibit significant negative solvatochromism in solution. Heterogeneous reactions between hot aqueous solutions of Tl₂CO₃ and solid protonated 2-heteroarylcyanoximes HL afford yellow TlL. The crystal structure of Tl(BTCO) shows the formation of centrosymmetrical dimers, which connect with each other to form a double-stranded one-dimensional coordination polymer. The oxygen atom of the oxime group acts as a bridge between the three different Tl(I) centers. The anion is non-planar and adopts a *trans-anti* configuration in the complex. The polymeric motif in the complex represents a ladder-type structure. Staggered π - π interactions between benzothiazolyl groups provide additional stabilization of the structure. Both organic ligands and their Tl(I) complexes exhibit strong room temperature blue emission in the solid state.

Introduction

The continuous interest in one-dimensional coordination polymers is primarily focused on molecular electronic devices¹ and the development of new luminescent materials.² Dimeric, trimeric, 3D-polymeric metal compounds and clusters with metallophilic interactions were found to exhibit photophysical properties useful for optoelectronics, such as metal-based room temperature luminescence,3 phosphorescence and vaporochromism.4 The latter property attracts attention due to the possibility of making new types of sensors for a variety of vapors of organic substances including industrial solvents⁵ and organophosphorous compounds.⁶ Light-emitting properties of heavy metal complexes and phosphorescence specifically, has been intensively studied in recent years due to their applications in high performance organic light emitting diodes (OLED).7 In fact, phosphorescence can lead to almost 100% internal quantum efficiency providing high external light output of the actual device. This approach shifted focus to the investigation of heavy metal complexes as phosphorescent materials since strong spin-orbit coupling induced by the heavy metal facilitates $S_n \rightarrow T_n$ intersystem crossing and allows strong phosphorescence at room temperature.⁸ The emission color of the system can be tuned by the introduction of various substituents on the ligand binding site,⁹ or by different auxiliary ligands.¹⁰ It should be noted especially that pure blue emitting materials are in great demand for application in full-colored LCD displays¹¹

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[†] Electronic supplementary information (ESI) available: Preparation of HBOCO and HQCO ligands, S1; tabulated room temperature ¹³C NMR spectra of all five synthesized benz-(2-heteroaryl)cyanoximes in DMSO-d₆, S2-S4; solid state IR spectroscopic data for HL and TIL (S5, S6); photographs of crystals of the cyanoxime ligands (S7) and their Tl-complexes (S20); details of crystal packing in the structure of HBOCO, S8-S10; linear correlations between UV-visible spectra, pK_a of the ligands and Hammett constants for the benz-(2-heteroaryl)cyanoximes, S11, S12; actual NMR spectra of HBTCO, HBIMCO and HBIHCO ligands, S13, S14; data of solution electrical conductivity studies, S15; UV-visible spectra of some of the protonated and deprotonated cyanoxime ligands, S16; correlations for solvatochromic series of the BOCO- anion, S17; typical fluorescence spectra of HL and NaL and signals deconvolution, S18; fluorescence of HBIHCO in EtOH solution, S19; solid state UV-visible spectra for TlL, S21; experimental setup for solid state fluorescence measurements, S22; emission spectra of TlL at different excitations, S23-S23. CCDC reference numbers 680405-680407. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b803846e

[‡] Dedicated to Prof. Vladimir Amirkhanov (Kiev State University, Ukraine) on the occasion of his 50th birthday.

since this color is much more difficult to generate than the other two (red and green) principal colors. Coordination polymers offer significant advantages over conventional molecular compounds due to very low solubility in conventional organic solvents and

water, and much higher thermal stability. There are two important factors that guide the search for onedimensional coordination polymers that may exhibit interesting photophysical properties. These are: 1) design and exploration of new bridging ligand systems that may provide the formation of well-organized one-dimensional polymeric motifs such as columns, chains and double strands (ladders) connected by nonbonding interactions; 2) the search for close spatial location of identical (in homometallic complexes) or different metals (in heterometallic complexes) in the crystal lattice due to direct metal-metal interactions, or appropriate bridging atoms/groups. Typically, coinage metals such as Cu,12 Ag,13 Au14 and Pt15 in homometallic and mixed-metal¹⁶ compounds are employed for building coordination polymers. Thallium has attracted special interest in recent years due to its pronounced ability to cause metallophilic interactions^{17,18} and the formation of metal-metal bonds with the above metal ions.^{4a,5a,19}

Since ligands were found to play a major role in the formation of coordination polymers with close metal-metal separations, our attention turned to cyanoximes - a new versatile group of stable organic molecules²⁰ with the general formula NC-C(=NOH)-R, where R represents a variety of electron-withdrawing groups. Recently, we reported the synthesis, spectroscopic properties and structures of a large group of Tl(I) complexes based on monosubstituted arylcyanoximes.²¹ These complexes have shown interesting double-stranded, ladder-type one-dimensional polymeric structures with short Tl-Tl distances comparable to that in metallic thallium (3.42 Å). Amongst all cyanoximes, heteroarylcontaining ligands attract special attention due to the presence of donor atoms other than nitrogen such as O,²² S²³ and Se,²⁴ and the ability to provide extra-stabilization of formed lattices because of the π - π stacking interactions. In general, 2-benz(heteroaryl) groups²⁵ are increasingly frequently incorporated into a variety of ligands that form interesting metal complexes. However, complexes of monovalent thallium with oximes and heterocyclic cyanoxime ligands in particular are insufficiently studied.

We report in our present paper the synthesis, spectroscopic and structural characterization of a series of benz(2-heteroaryl) cyanoximes as a new ligand system, and their thallium(I) complexes.

Experimental

Synthesized benz(2-heteroaryl)cyanoximes with their commonly used abbreviations²⁶ are shown in Scheme 1.

Materials and methods

Starting materials, thallium(I) carbonate, glacial acetic acid, sodium nitrite and substituted heteroaryl-actonitriles R–CH₂–CN (R = 2-benzothiazolyl, 2-benzimidazolyl, *N*-methyl-2-benzimidazolyl groups) were obtained from Aldrich and were used without additional purification. Precursors for HBOCO and HQCO ligands were obtained using a three-step procedure^{26,27} depicted in the electronic supplementary information (ESI).†Organic solvents



(Spectrum Chemicals, J. T. Baker) were of HPLC grade and used without additional distillation. Melting points or decomposition temperatures for synthesized protonated cyanoximes and their Tl(1) salts were determined using Mel-Temp apparatus (Thomas Hoover). TLC was carried out on silica coated glass plates (Merck) containing a fluorescent indicator. Elemental analyses on C,H,N content were performed at the Atlantic Microlab (Norcross, GA).

Spectroscopy

All synthesized organic ligands were characterized at 296 K using ¹H, ¹³C NMR, COSY and HMQC spectroscopy (solutions in DMSO-d₆ and acetone-d₆; TMS was an internal standard; Varian INova 400 MHz spectrometer). The UV-visible spectra of protonated ligands HL and their tetrabutylammonium salts or Cs⁺ salts were recorded at room temperature (293 K) on an HP 8354 spectrophotometer in the range 200-1100 nm, using 1 mm and 10 mm quartz cuvettes (Starna, Inc.). Room temperature (294 K) solid state absorbance spectra of the Tlcyanoximates were recorded at the same wavelength intervals from fine suspensions in silicon oil squeezed between two 10 \times 40×1 mm quartz plates. Solution fluorescence spectra of HL, deprotonated anionic cyanoximes (as NaL), and TlL (L = studied cyanoxime ligands) were obtained at 293 K using a Shimadzu RF-5301 PC spectrofluorometer in the range 200-900 nm. Fluorescence lifetime measurements at 296 K were carried out on a Jobin Ivon Fluorolog system using LEDs of variable wavelengths as excitation sources. Photoluminescence from solid samples was measured at 294 K using pressed fine powders of studied cyanoximates (page S22, ESI[†]). Infrared spectra were recorded in the range 500-4000 cm⁻¹ using the FT IR Nicolet Magna 550 spectrophotometer using a KBr matrix for protonated cyanoximes HL and their cesium salts CsL. However, the IR spectra of TlL were obtained from fine suspensions in Nujol due to the solid state exchange reactions between KBr and TlL during pellet preparation. A mass-spectrometric characterization (positive FAB) of the protonated 2-heteroarylcyanoximes was carried out using Autospec Q and ZAB Finigan spectrometers. meta-Nitrobenzylic alcohol, NBA, was used as a matrix in all experiments.

Solution studies

Electrical conductivity of 1 mM solutions of HL (in anhydrous acetone, DMSO and DMF), CsL and TlL (in DMSO and water; L = studied cyanoxime anions) was measured at 295 K using the YSI Conductance-Resistance meter Model 34. Solutions

of tetrabutylammonium bromide and tetraphenylphosphonium bromide (as 1 : 1 electrolytes) were used for the electrode calibration. Measurements of pK_a values for synthesized benz(2-heteroaryl)cyanoximes were carried out using a Sirius Analytical Instruments automated titration station (Sussex, UK) equipped with a temperature-controlled bath. Since protonated cyanoximes HL are poorly soluble in water, all measurements were conducted in mixed solvent systems using DMSO as solubilizing co-solvent. AtenololTM and LidocaineTM (from Aldrich) were used for calibration of the instrument. Measurements consisted of three-step multi-stage titrations in water–DMSO mixtures from 20 wt% to 30 wt% with ionic strength adjusted to 0.15 with KCl. The values were extrapolated to "zero" DMSO content to obtain an aqueous pK_a value using the Yasuda–Shedlovsky procedure. The pH in titration experiments ranged from 3 to 11.

X-Ray crystallography

Crystal structures were determined for two protonated 2heteroarylcyanoximes (HBIMCO, HBOCO) and one monovalent thallium complex Tl(BTCO). Suitable quality single crystals of organic ligands were obtained upon slow evaporation of their water–ethanol or water–acetone solutions at room temperature. X-Ray quality single crystals of the thallium(I) complex were obtained upon the slow cooling (~28 h) of a hot aqueous solution of Tl(BTCO) in a thermostat. Data collection for the studied crystals was carried out at low temperature using either a Bruker SMART CCD diffractometer operating in ω-scans mode or a Stöe IPDS-II imaging plate diffractometer. The X-ray source was a fine focused sealed Mo tube (K_{α} radiation; $\lambda = 0.71070$ Å; highly oriented graphite monochromator). The data were corrected for decay and absorption using either X-RED or the SADABS 30 program.²⁸ Direct methods structure solution, difference Fourier calculations, and full-matrix least squares refinements against F^2 were performed with a SHELXL-97 program package. All non-hydrogen atoms were refined with anisotropic displacement parameters, while hydrogen atoms were placed in geometrically idealized positions and refined using a riding model. The crystal and refinement data for the studied compounds are listed in Table 1, while selected bond lengths and valence angles in the structures are presented in Table 2. An ORTEP program package²⁹ was used to draw figures of crystal structures. The respective cif files are available in the ESI.[†]

Synthesis of benz-(2-heteroaryl)cyanoximes

The preparation of these compounds was accomplished using the modified Meyer reaction³⁰ shown in Scheme 2. This route represents nitrosation reaction in glacial acetic acid^{26,31} and leads to the desired 2-heteroarylcyanoximes with 80–95% yields. Since all preparations of the protonated cyanoximes HL described here are similar, synthesis of only one ligand – H(BIHCO) – will be presented in detail.

 α -Oximino-(2-benzimidazolyl)acetonitrile, HBIHCO. Benzimidazolyl-2-acetonitrile, C₇H₄N₂-CH₂-CN (1 g, 6.4 mM) was placed in a heavy walled 50 mL round bottom flask with a

 Table 1
 Crystal and refinement data for synthesized 2-heteroarylcyanoximates

Parameter	HBIMCO·H ₂ O	H ₂ BOCO ⁺ BOCO ⁻	Tl(BTCO)
Empirical formula	$C_{10}H_{11}N_4O_2$	C ₀ H ₅ N ₃ O ₂	C ₀ H ₄ N ₃ OSTl
Formula weight	219.23	374.32	406.58
Temperature/K	150 (2)	173 (3)	150 (2)
Crystal dimensions/mm	$0.15 \times 0.12 \times 0.1$	$0.50 \times 0.30 \times 0.05$	$0.15 \times 0.07 \times 0.06$
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	<i>P</i> -1	$P2_1/c$	$P2_1/c$
Unit cell dimensions:			
a/Å	7.1446(18)	14.1723(19)	14.8621(17)
b/Å	8.587(2)	7.1591(10)	4.4277(3)
c/Å	8.988(2)	17.461(2)	15.0453(15)
$\alpha/^{\circ}$	96.67(2)	90.00	90.00
$\beta/^{\circ}$	109.370(18)	101.404(2)	90.15(9)
$\gamma/^{\circ}$	99.79(2)	90.00	90.00
Volume/Å ³	503.7(2)	1736.7(4)	990.05(16)
Z	2	4	2
Density (calc.)/Mg m ⁻³	1.445	1.432	2.728
Absorption coeff./mm ⁻¹	0.105	0.106	16.496
F(000)	228	768	736
Theta range for data/°	3.10 to 34.75	1.47 to 27.13	2.71 to 34.78
Index ranges:			
	-11 < h < 11	-18 < h < 14	-23 < h < 23
	-13 < k < 13	-9 < k < 9	-5 < k < 7
	-14 < l < 14	-22 < l < 22	-24 < l < 24
Reflections collected	13006	11651	19093
Independent reflections	4301	3815	4236
$R_{\rm int}$	0.0692	0.0846	0.0950
Completeness to theta (%)	98.5 (at 34.75°)	99.3 (at 27.13°)	99.1 (at 34.78°)
Goodness of fit	1.012	1.027	1.042
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0562, wR_2 = 0.1389$	$R_1 = 0.0708 \text{ w} R_2 = 0.1706$	$R_1 = 0.0637 \text{ w} R_2 = 0.1698$
R indices (all data)	$R_1 = 0.1169 \text{ w} R_2 = 0.1687$	$R_1 = 0.2128 \text{ w} R_2 = 0.2406$	$R_1 = 0.0843 \text{ w} R_2 = 0.1888$
Extinction coefficient	0.084(17)	0.0018(13)	0.0144(12)
Highest peak/hole/A ⁻³	0.367/-0.364	0.798/-0.543	3.949/-2.528

Table 2 Selected^a bond lengths (Å) and valence angles (°) in the structures of synthesized 2-heteroarylcyanoximes

Compound	Bonds		Angles	
HBIMCO H ₂ O	C(1)–N(1)	1.322(2)	N(1)–C(1)–N(2)	113.23(13)
- u c ¹⁰	C(1) - N(2)	1.366(2)	N(1) - C(1) - C(2)	121.25(13)
н ₃ С	C(1) - C(2)	1.460(2)	N(2) - C(1) - C(2)	125.52(13)
N_{λ}^{4}	C(2) - N(3)	1.286(2)	N(3) - C(2) - C(3)	120.93(14)
N^{-5}	C(2) - C(3)	1.453(2)	N(3)-C(2)-C(1)	122.55(14)
	C(3) - N(4)	1.142(2)	C(3)-C(2)-C(1)	116.48(13)
	C(4) - N(1)	1.383(2)	N(4) - C(3) - C(2)	177.96(17)
	C(5) - N(2)	1.384(2)	C(1) - N(1) - C(4)	105.17(12)
$H \cup N \qquad N \qquad 4 \checkmark$	N(3) - O(1)	1.3629(19)	C(1) - N(2) - C(5)	106.36(12)
			C(2) - N(3) - O(1)	111.61(13)
BOCO ⁻ molecule a nitroso-anion	O(1a)-C(1a)	1 356(5)	C(1a)=O(1a)=C(2a)	103 4(3)
3a	O(1a) - C(2a)	1 399(5)	C(1a) - N(1a) - C(7a)	104.5(4)
	N(1a) - C(1a)	1.296(6)	N(1a) - C(1a) - O(1a)	115 9(4)
Č 9a	N(1a)-C(7a)	1.404(6)	N(1a) - C(1a) - C(8a)	127.7(4)
	C(1a)-C(8a)	1.428(6)	O(1a) - C(1a) - C(8a)	116.3(4)
8a II	O(2a)-N(2a)	1.259(6)	O(2a) - N(2a) - C(8a)	103.4(5)
	C(2a)-C(7a)	1.377(6)	C(9a)-C(8a)-C(1a)	120.8(4)
2a 2a 1a	N(2a)-C(8a)	1.444(7)	C(9a)-C(8a)-N(2a)	127.5(4)
	N(3a)-C(9a)	1 149(6)	C(1a) - C(8a) - N(2a)	111.5(4)
	C(8a) - C(9a)	1.421(7)	N(3a) - C(9a) - C(8a)	179 0(5)
			N(2a) - O(2a) - H(2a)	109.5
H_2BOCO^+ molecule <i>h</i> oxime cation	O(1b) = C(1b)	1 363(5)	C(1b) = O(1b) = C(2b)	104.2(3)
	O(1b) - C(2b)	1 397(5)	C(1b) = N(1b) = C(7b)	105.3(4)
	N(1b)-C(1b)	1.288(5)	N(1b) - C(1b) - O(1b)	114 8(4)
C 9b (+) N 7b	N(1b) - C(7b)	1.402(5)	N(1b) - C(1b) - C(8b)	127.4(4)
	C(1b)-C(8b)	1.439(6)	O(1b) - C(1b) - C(8b)	117.7(4)
	O(2b) - N(2b)	1.352(4)	C(8b) - N(2b) - O(2b)	112.2(4)
	C(2b)-C(7b)	1.377(6)	N(2b) - C(8b) - C(9b)	121.5(4)
2b $2b$ $2b$ $2b$	N(2b)-C(8b)	1.294(6)	N(2b)-C(8b)-C(1b)	118.6(4)
1 0	N(3b) - C(9b)	1.137(6)	C(9b) - C(8b) - C(1b)	119.8(4)
	C(8b)-C(9b)	1.430(6)	N(3b)-C(9b)-C(8b)	177.2(5)
			N(2b) - O(2b) - H(2b)	109.5
Tl(BTCO) ^c	C(1) - N(1)	1.297(11)	N(1)-C(1)-C(2)	125.4(9)
3	C(1) - C(2)	1.441(14)	N(1) - C(1) - S(1)	116.3(8)
	C(1) = S(1)	1.763(10)	C(2)-C(1)-S(1)	118.2(6)
	C(2) - N(2)	1.319(10)	N(2)-C(2)-C(3)	120.8(8)
	C(2) - C(3)	1.429(12)	N(2) - C(2) - C(1)	118.3(8)
	C(4) - C(5)	1.398(13)	C(3)-C(2)-C(1)	120.7(7)
0-N S 5	C(3) - N(3)	1.149(12)	N(3) - C(3) - C(2)	175.0(9)
	C(5)-S1	1.745(9)	C(1) - N(1) - C(4)	110.3(8)
Ť.	N(2) - O(1)	1.317(11)	C(2) - N(2) - O(1)	116.6(8)
''1	Tl(1)o-O(1) ^e 1	$2.859(7)^{b}$	C(5) - S(1) - C(1)	88.3(4)
	Tl(1)–O(1)	2.635(7) ^b	$O(1) - TI(1) - O(1)^{e}1$	107.3(2)
	$Tl(1) - O(1)^{c}2$	2.864(8)	$O(1) - Tl(1) - O(1)^{c}2$	76.2(2)

^{*a*} Geometry of the phenyl group adjacent to the heteraryl fragment is normal and not shown. ^{*b*} Details of geometry at the Tl(1) center are presented in Fig. S10 ESL. ^{*c*} Symmetry operations are for #1: x, y + 1, z; while for #2: -z - 1, -y - 1, -z + 1.



#19/38 taper joint, and dissolved in 5 mL of glacial acetic acid at 25 °C. Argon was slowly bubbled through the solution for 20 min to replace air. The purged solution was frozen using an ice bath. Solid NaNO₂ (0.8789 g; 12.7 mM, in excess) was added at once on top of the frozen solution and the flask was closed with a heavy-duty Teflon valve with a #19/38 taper joint. The reaction mixture was allowed to thaw slowly for 12 hours. Vacuum/inert gas flushing was applied prior to opening the flask in order to release any pressure buildup. 35 mL of water were poured into the reaction mixture, leading to the rapid precipitation of a pale yellow solid that was filtered, washed with 100 mL of water (3 portions), and dried in a vacuum dessicator charged with NaOH pellets. Recrystallization with charcoal afforded a white solid; yield: 1.164 g (98%). $R_{\rm f} = 0.78$ (pure EtOAc) and 0.53 in EtOAc-hexane = 4: 1. Upon heating, the color changed to yellow at 230 °C followed by rapid decomposition to a brown, tarry product at 280 °C. IR spectrum (cm⁻¹): 3345 v(NH); 3284 v(OH); 3061 v(C-H) arom; 2239 v(C≡N); 1614 v(C=N) ring; 1533 v(C=N) oxime; 1065 v(N-O). HBIHCO in DMSO-d₆ solution at 298 K represents a mixture of syn- (36%) and anti- (64%) isomers. The latter isomer also exhibits a dynamic prototropic tautomeric equilibrium, which is discussed later in this paper. ¹H NMR (ppm) data for syn-isomer: 14.35 (1H, broadened OH), 13.14 (1H, broad Other benz-(2-heteroaryl)cyanoximes follow:

a-Oximino-(*N*-methyl-2-benzimidazolyl)acetonitrile, HBIMCO. White solid, 95% yield; color change upon heating begins at 195 °C with rapid decomposition to a brown, tarry product at 235 °C; $R_f = 0.72$ (EtOAc-hexane = 4 : 1). IR spectrum (cm⁻¹): 3570 v(OH); 3023 v(C–H) arom; 2940 v^{as} (C–H), 2790 v^{s} (C–H) methyl; 2236 v(C \equiv N); 1610 v(C=N) ring; 1596 v(C=N) oxime; 1090 v(N–O). Mixture of two isomers (25% *syn*- and 75% *anti*-) in DMSO-d₆ solution at 297 K. ¹H NMR (ppm) for dominant *anti*-isomer: 14.45 (OH oxime, 1H broadened singlet), 7.73 (2H, doublet), 7.63 (2H, doublet), 7.36 (2H, triplet), 7.27 (2H, triplet), 3.94 (3H, methyl group). High-resolution mass-spectrometry: calc for C₁₀H₈N₄O, 200.0698; found, 201.0763 (M + 1). The compound crystallizes as monohydrate, and clear HBIMCO × H₂O needles suitable for X-ray analysis were obtained after the slow evaporation of a water–ethanol solution at 4°C (page S7, ESI†).

α-Oximino-(2-benzoxazolyl)acetonitrile, HBOCO. Brown solid, yield 86%; melting with decomposition at 195 °C; $R_f = 0.53$ (EtOAc–hexane= 1 : 1). IR spectrum (cm⁻¹): 3433 v(OH); 3100 v(C–H) arom; 2243 v(C≡N); 1612 v(C=N) ring; 1585 v(C=N) oxime; 1045 v(N–O). Compound represents a mixture of *syn-* (10%) and *anti-* (90%) isomers in DMSO-d₆ solution. ¹H NMR (ppm) for *anti-*isomer: 14.05 (1H, broad oxime OH singlet), 7.85 (1H, doublet), 7.79 (1H, doublet), 7.50 (1H, triplet), 7.46 (1H, triplet). High-resolution mass-spectrometry: calc for C₉H₅N₃O₂, 186.0542; found, 187.0628 (M + 1). Brown clear blocks of **HBOCO** were grown during the slow evaporation of its acetone–water solution at 4 °C.

a-Oximino-(2-benzothiazolyl)acetonitrile, HBTCO. Tanyellow solid, yield 90%; color change upon heating begins at 205 °C with rapid decomposition to brown, tarry product at 221 °C; $R_f = 0.30$ (EtOAc-hexane= 1 : 1). IR spectrum (cm⁻¹): 3240, 3159 v(OH); 3075 v(C-H) arom; 2263, 2235 v(C=N); 1590, 1556 v(C=N) ring, 1575 v(C=N) oxime; 1063 v(N-O). The compound represents a mixture of *syn*- (10%) and *anti*-(90%) isomers in DMSO-d₆ solution. ¹H NMR (ppm) for major isomer: 14.82 (1H, broad oxime singlet), 8.11 (2H, multiplet: two overlapped doublets), 7.54 (2H, multiplet: two overlapped triplets). High-resolution mass-spectrometry: calc for C₉H₅N₃OS, 203.0153; found, 204.0211 (M + 1).

a-Oximino-(2-quinolyl)acetonitrile, HQCO. White solid, yield 87%; melting with decomposition at 184 °C; $R_f = 0.38$ (EtOAc-hexanes= 1 : 2). IR spectrum (cm⁻¹): 3550 v(OH); 3030 v(C–H) arom; 2230 v(C=N); 1596 v(C=N) ring, 1615 v(C=N) oxime; 1030 v(N–O). Compound represents a mixture of *syn-* (13%) and *anti-*(87%) isomers in acetone-d₆ solutions at 297 K. ¹H NMR (ppm) data for dominant isomer: 13.15 (1H, broadened oxime singlet), 8.43 (1H, doublet), 8.14 (1H, doublet), 8.05 (1H, doublet), 8.03 (1H, doublet), 7.86 (1H, triplet), 7.70 (1H, triplet). High-resolution mass-spectrometry: calc for C₁₁H₇N₃O 197.0589; found, 198.0694 (M + 1).

¹³C NMR spectra for all protonated cyanoximes HL reported in this paper are tabulated in pages S2–S4 of the ESI.† All synthesized organic compounds are microcrystalline powders, soluble in light alcohols ROH, acetone, CH_3CN , ether, ethyl acetate and pyridine (with the formation of ionic salts), but were sparingly soluble in water and CCl_4 , and insoluble in hexane and aromatic hydrocarbons.

Synthesis of thallium(I) complexes

There are three practical routes for the synthesis of Tl(1) derivatives of weak organic acids (Scheme 3). Route 1 represents a clean heterogeneous reaction that results in the evolution of CO_2 , which drives the reaction to completion. Crystals suitable for X-ray analysis can be obtained upon slow cooling of a hot filtered reaction mixture in a thermostat. We successfully used all three routes during years of investigation of Tl(1) cyanoximates in the past. However, this method 1 was employed in this report, since it combined reasonable speed of preparation with a good chance of getting X-ray quality crystals. The typical synthesis of one complex is described below.



Thallium(1) α-oximino-(2-benzoxazolyl)acetonitrile, Tl(BOCO). Thallium(1) carbonate, Tl₂CO₃ (250.5 mg; 0.53 mM) was dissolved under stirring in 10 mL of water at 96 °C. Small portions (200.0 mg; 1.06 mM) of solid HBOCO ligand were added within 2 minutes to a boiling aqueous solution of thallium(1) carbonate. When all CO₂ was evolved, a slightly cloudy solution was hot filtered using a jacketed, steam heated filter funnel into a large pyrex test tube that was immersed and fixed inside a Dewar flask containing five liters of water preheated to 95 °C. Slow cooling of the mother liquor over several days afforded long fibrous golden crystals of the Tl(BOCO) complex. The compound was filtered and dried in a dessicator under P₄O₁₀. Yield: 214.2 mg (50%); mp ~ 180 °C (dec.). Anal. for C₉H₄N₃O₂Tl calculated (found), %: C 27.68 (27.22), H 1.03 (1.20), N 10.76 (10.56).

Other thallium(I) cyanoximates follow.

Thallium(I) α-oximino-(2-benzothiazolyl)acetonitrile, Tl(BT-CO). Yield 72%; at ~190 °C complex decomposes. Anal. for $C_9H_4N_3OSTI$ calculated (found), %: C 26.59 (26.27), H 0.99 (1.11), N 10.33 (10.38).

Thallium(1) α-oximino-(2-benzimidazolyl)acetonitrile, Tl(BI-HCO). Yield 40%; at ~140 °C complex decomposes. Anal. for $C_9H_5N_4OTl$ calculated (found), %: C 27.75 (27.75), H 1.29 (1.25), N 14.38 (14.12).

Thallium(I) α-oximino-[(*N*-methyl)-2-benzimidazolyl]acetonitrile, Tl(BIMCO). Yield 42%; at ~160 °C complex decomposes. Anal. for $C_{10}H_7N_4$ OTl calculated (found),%: C 29.76 (29.95), H 1.75 (1.73), N 13.88 (13.86). Thallium(I) α-oximino-(2-quinolyl)-acetonitrile, Tl(QCO). Yield 75%; at ~140 °C complex decomposes. Anal. for $C_{11}H_6N_3$ OTl calculated (found), %: C 32.98 (32.56), H 1.51 (1.48), N 10.49 (10.19).

All five obtained monovalent Tl cyanoximates represent yellow crystalline compounds that are not soluble in ether, ethanol, propanol, chlorohydrocarbons or aromatic hydrocarbons, but dissolve in CH₃CN, DMF, DMSO, pyridine and hot water. The IR spectra of synthesized Tl(1) complexes are tabulated in pages S5 and S6 in the ESI.† All synthesized Tl(1) benz-(2-heteroaryl)cyanoximates form fibrous or needle-type crystals (p. S20 ESI†).

SAFETY NOTE! Although we have not encountered any problems during many years of laboratory work and handling, special care should be taken during procedures using thallium compounds because of their toxicity.

Results and discussion

Characterization of the ligands

Solid state structure of HBIMCO \cdot H₂O. The molecular structure of this 2-heteroarylcyanoxime is displayed in Fig. 1, while values for bonds and valence angles are presented in Table 2. HBIMCO crystallizes as a monohydrate similarly to the 2quinolylcyanoxime, HQCO ligand.³¹ Contrary to the latter, HBIMCO adopts a planar trans-anti configuration. Crystallization water molecules play an essential role in packing of the cyanoxime into the crystal. A system of H-bonds is formed between the nitrogen atom of the imidazolyl group and the oxygen atom of the oxime group (Fig. 1) with parameters: N1-H1w-Ow =1.853 Å, $\angle N1$ -H1w-Ow = 173.3°, Ow-H1(oxime) = 1.617 Å with $\angle Ow-H1(\text{oxime})-O1 = 161.2^{\circ}$. Therefore, water molecules connect to translation-related HBIMCO molecules along the y axis into a planar sheet. Formed sheets are held together by "headto-tail" π - π stacking interactions at 3.35 Å along the *x* direction (Fig. 1). A series of distances between two neighboring molecules forming π - π stacks in the structure of HBIMCO are the following: centroids of the phenyl rings are separated by 7.043 Å, while centroids of the imidazole rings are separated by 4.147 Å. The distance between centroids of the phenyl group and imidazole ring is 5.375 Å. Geometrical parameters of the cyanoxime fragment are



Fig. 1 Fragment of crystal packing and numbering scheme in the structure of $HBIMCOxH_2O$ showing one layer of molecules in the unit cell. A – side view that displays the H-bonded chain of the heterocyclic cyanoxime; B – orthogonal view shows the ligand's planarity.

normal for this class of compounds.^{21,31,41} Bond lengths and valence angles in the heterocyclic fragment of the molecule are normal for the aromatic compounds as well.

Crystal structure of HBOCO. 2-Benzoxazolylcyanoxime, HBOCO, is a colored substance contrary to other analogous cyanoxime molecules described in this paper (S7 ESI[†]) or substituted arylcyanoximes.²¹ This is highly unusual since the vast majority of oximes (and cyanoximes in particular) are colorless. The solid-state structure of HBOCO is unique among all known cyanoximes.³¹ The molecular structure of this compound is shown in Fig. 2, while bond lengths and valence angles are presented in Table 2. The unit cell contains two crystallographically different HBOCO molecules, a and b, that form H-bonded dimeric units (Fig. 2). Both molecules a and b are practically planar, but



Fig. 2 Atomic numbering scheme in the structure of the HBOCO dimer: cationic molecule a is in *cis-anti* configuration, while anionic molecule b adopts *trans-anti* configuration. A – top view, B – side view (~90° rotation) of the dimer showing dihedral angle between two planar cyanoxime molecules.

have different geometrical configurations: cis-anti and trans-anti respectively. The dihedral angle between planes of *a* and *b* molecules in the dimer is 45.85°. There is a significant difference in the geometry of the oxime fragment in both molecules (Table 2). Thus, molecule a has typical geometry for the *nitroso*-anions³² showing a much shorter N2a-O2a than C8a-N2a distance in the group (Fig. 2). However, molecule b is an oxime (Table 2). It is commendable that there are unusually large thermal ellipsoids for N2a and O2a atoms in the molecule a (Fig. 2). This is evidence of their significant thermal motion as anionic nitrosogroup which is weakly H-bound to the typical protonated cationic oxime molecule b. These geometrical features, combined with the intense brown color for the compound, confirm formation of the cation-anion pair $H_2BOCO^+ \cdots BOCO^-$ (Scheme 4). This autoionization is also reflected in the $n \rightarrow \pi^*$ transition at ~390 nm – which is typical for anionic cyanoximates - in the solid state spectrum of HBOCO. This is an interesting example of an intermolecular proton transfer leading to autoionization, which is a fast process,³³ while the X-ray structure reflects the averaged equilibrated position of the involved atoms. Crystal packing of HBOCO is also quite unusual among all the cyanoximes studied to date.^{21,31} Extensive intermolecular H-bonding and short π - π stacking "head-to-tail" interactions at 3.36 Å are responsible for the formation of interesting lattice architecture (S8-S10 ESI⁺). The series of distances between the two π - π stacked molecules *a* and b in the structure of HBOCO is the following: centroids of the phenyl ring a and phenyl ring b are separated by 3.581 Å, centroids of the oxazole ring a and oxazole ring b are separated by 4.775 Å, while centroids of the oxazole ring a and phenyl ring **b** are separated by 3.588 Å with centroids of the phenyl ring **a** and oxazole ring **b** being 3.868 Å apart.



Acid-base properties of benz-(2-heteroaryl)cvanoximes in solution. Synthesized 2-heteroarylcyanoximes represent monoprotic acids that are significantly more acidic than aliphatic monoximes and dioximes.³⁴ The values of measured pK_a for HQCO, HBOCO, HBTCO, HBIHCO and HBIMCO together with literature data for related compounds are presented in Table 3. Thus, HBOCO is ~12 900 times more acidic than its analogous benz-(2oxazolyl)aldoxime (Table 3). The value of pK_a for the oxime proton in HBOCO is 4.66 ± 0.01 and represents the highest acidity of the oxime group among the studied 2-heteroarylcyanoximes. The heterocylic nitrogen atoms in HBOCO, HBTCO, HBIMCO and HBIHCO could not be protonated under the studied conditions in mixed aqueous-DMSO (21-35 wt%) solutions with pH ranging from 3 to 11. This finding is a surprise in the light of the existence of transition metal complexes with 2-heteroarylcyanoximates where the latter act as chelating ligands,³⁵ offering the heterocyclic nitrogen atom for coordination. Nevertheless, the nitrogen atom

Table 3 Values of pK_a for several cyanoximes and related compounds

Compound	pK_{a1} , oxime	pK_{a2} , other sites	Reference
HO-N N	4.66	<i>a</i>	This work
НВОСО			
HO-N N	8.77	<i>a</i>	55
NC S	5.05	a	This work
НВТСО			
H3C HO-N N	5.66	a	This work
HBIMCO			
	6.44	8.65-azomethyne group, C=N	55
NC N HO-N N	5.84	3.38-acidic NH group	This work
HBIHCO			
	6.18	10.29	This work
HQCO			

^{*a*} No protonation of the heterocyclic nitrogen atom was observed in the studied pH range in DMSO–H₂O systems.

of the quinoline group in HQCO can be protonated: its pK_a was found to be 10.3 ± 0.01 (Table 3). The NH-proton in the HBIHCO is unexpectedly acidic with a measured $pK_a = 3.38 \pm 0.02$ for that group. A linear correlation between λ_{max} of the $n \rightarrow \pi^*$ transition in the *nitroso*-chromophore of anionic benz-(2-heteroarylcyanoximes) L⁻ in ethanol and pK_a values of the oxime group in HL was observed (S11 ESI†). Similarly, linear relationships between Hammett σ_p and σ_m constants³⁶ for the benz-(2-heteroaryl) fragments and pK_a values of the cyanoximes were found as well (S12 ESI†).

Solution structure: NMR spectra. Benz-(2-heteroaryl)cyanoximes exhibit rich stereochemistry and exist as several geometrical isomers, while their *nitroso*-counterparts exhibit free rotation around the C–N bond (Scheme 5) reducing the number of possible species in solution. ¹³C NMR spectra of all synthesized compounds in DMSO-d₆ and acetone-d₆ contain a double set of signals (S13, S14 ESI†). This is due to the presence of the two *syn*- and



Scheme 6

anti-geometrical oxime isomers in solution for HBIMCO, HBOCO, HBTCO, and prototropic tautomerism combined with the presence of the two isomers for solutions of HBIHCO (Scheme 6). Partial autoionization with the formation of zwitterionic species takes place in solutions of HQCO (S15 ESI[†]).

HBOCO forms a yellow solution in DMSO-d₆ and exists as a mixture of the *trans-anti* (dominant, 90%) and *trans-syn* isomers at room temperature according to ¹H NMR spectroscopy data. Benz-(2-oxazolyl)cyanoxime is only slightly ionized in solution, contrary to the prediction one could make from the X-ray structure, which confirmed the autionization of HBOCO in the solid state. ¹H NMR spectra of HBIMCO and HBTCO in DMSO-d₆ indicated

the presence of 27% syn-/73% anti- and 12% syn-/88% antiisomers in the mixture respectively (S13, S14 ESI†). Nevertheless, as discussed earlier, HBIMCO and HBTCO crystallize exclusively as *trans-anti* isomers in a solid state. Both ¹H and ¹³C NMR spectra of HBIHCO in DMSO-d₆ at 298 K demonstrate the presence of the two geometrical isomers (S14 ESI†), where the *anti*-isomer is involved in a prototropic tautomeric equilibrium as depicted in Scheme 6. H-bonding is essential for "locking" the *syn*-isomer from conversion into an *anti*-isomer and significantly slows tautomerism, leading to six narrow ¹³C signals in the spectra that evidenced the equivalence of three carbon atoms in the phenyl ring (S14 ESI†).



We found that the HBIHCO tautomeric equilibrium is sensitive to temperature, but is independent of concentration, suggesting an intramolecular process. A similar case of tautomerism for the benz-(2-imidazolyl)aminomethyl ligand has been recently reported in its *tris*-Co(III) complex.³⁷ The HQCO forms brightyellow solutions in acetone-d₆ and DMSO-d₆ and exists as a mixture of *trans-anti* (dominant, 88% in the former solvent) and *cis-syn* isomers at room temperature according to ¹H NMR spectroscopy data. The latter isomer is stabilized due to the formation of an intramolecular H-bond and prone to autoionization because of the favorable geometry in this pseudocyclic structure:

Indeed, both UV-visible spectra and the solution electrical conductivity studies (see below and S15 ESI†) have confirmed the formation of ionic species. The cyanoxime anions exhibit the characteristic $n \rightarrow \pi^*$ transition in the >CNO chromophore³⁸ at ~380–450 nm, while protonated HL compounds are colorless. The ¹³C NMR spectra of HQCO in acetone-d₆ and DMSO-d₆ show only a double set of signals that correspond to only two isomers in solution. Proton migration is a fast process and can't be investigated by NMR spectroscopy: there was only one significantly broadened symmetrical signal of the oxime hydrogen observed at ~14 ppm. Interestingly, HQCO monohydrate crystallizes as a single *trans-anti* isomer.³¹

Solution conductivity studies. Electrical conductivity of 1mM solutions of all studied benz-(2-heteroaryl)cyanoximes in acetone, DMF and DMSO was measured at 298 K and the results tabulated in S15 ESI.† Thus, HBIHCO, HBTCO and HBIMCO do not form conductive and colored solutions in the studied polar aprotic solvents. Solutions of HBOCO show a small degree of conductivity in these solvents (S15 ESI†). Solutions of HQCO are significantly more conductive, which implies a larger degree of autoionization and confirm the formation of the yellow colored anionic species. Thus, approximately 5–20% of the ionic species formed in acetone, DMF and DMSO solutions (S15 ESI†).

UV-visible spectra. With the exception of the pale-yellow HBTCO and the brown HBOCO, other obtained benz-(2heteroaryl)cyanoximes HBIMCO, HBIHCO, HQCO are colorless in the solid state. As mentioned before, the deprotonation of cyanoximes with bases in aqueous solutions or organic solvents leads to the formation of yellow/orange colored planar conjugated anions with a substantial charge delocalization.³⁹ The latter is reflected in the bathochromic shift of bands in the UV-visible spectra²¹ of anions L⁻ as compared to protonated HL species (S16 ESI[†]). Color in the anionic species originates due to the $n \rightarrow \pi^*$ transition in the NO-chromophore,38,40 where the values of the extinction coefficient range between 10 to 200 M⁻¹ cm⁻¹.^{21,41} UVvisible spectra of the studied cyanoxime anions are summarized in Table 4. As part of the characterization of the new ligand systems, we investigated both protonated forms HL and anionic species Lin solution using UV-visible spectroscopy. Positions of the bands in

Table 4Results of UV-visible spectroscopic studies of synthesized 2-heteroarylcyanoximates in EtOH solutions at 296 K

	$\lambda_{\rm max}/{\rm nm}~(\epsilon,{\rm M}^{-1}~{\rm cm}^{-1})$	
Cyanoxime anion	UV region ^a	Visible region ^b
BIHCO ⁻ , NBu₄ ⁺ salt	206 (45480); 269 (7400); 328 (25900)	~430 shoulder
BIMCO ⁻ , NBu ₄ ⁺ salt	204 (48100); 235 (10000); 321 (21700)	396 (139)
BOCO, NBu ₄ salt	202 (41800); 230 (11150); 326 (26300)	432 (109)
BTCO ⁺ , NBu₄ ⁺ salt	219 (20600); 249 (10000); 342 (18100)	423 (128)
QCO ⁻ , Cs⁺ salt	207 (14300); 235 (11200); 248 (12100) 306 (8740)	~410 shoulder

 a 1 mm quartz cuvette, 5 \times 10 $^{-4}$ M concentration. b 1 cm quartz cuvette, 5 \times 10 $^{-3}$ M concentration.

spectra of all benz-(2-heteroaryl)cyanoxime anions showed solvent dependence consistent with a negative solvatochromic effect.⁴² The solvatochromic series for solutions of the BTCO- anion (as tetrabutylammonium salt) are displayed in Fig. 3. Two groups of solvents are immediately seen in this plot: polar protic solvents ROH form one group of curves, while polar aprotic solvents strongly separated form the latter (Fig. 3). The energy difference between the two groups is ~9 kcal Mol⁻¹ and consistent with the formation of hydrogen bonds of medium strength. For all studied benz-(2heteroaryl)cyanoxime anions, solvent dependence of the $n \rightarrow \pi^*$ band position in visible spectra from pK_a of the solvent ROH, or its specific solvation Z parameter^{34,43} has linear character (S11, S12 ESI[†]). The typical correlation plots for NBu₄⁺BOCO⁻ in alcohols are presented in S17 ESI.† Previously we have reported a significant solvent dependence for other studied amide-41 and aryl-21 cyanoxime ligands. Detailed investigation and



Fig. 3 Solvatochromic series for isomolar (5 mM) solutions of **BTCO** anion in different solvents at 296 K (1 cm cuvette).

interpretation of this interesting phenomenon for cyanoxime anions will be presented in a separate publication.

Fluorescence spectra. Three out of five studied ligands exhibit strong blue fluorescence in solution (Fig. 4) with BIHCO being the strongest emitter (S19 ESI[†]). Signals in the overall spectroscopic envelope are centered at ~490 nm and possess a fine structure, which can be fitted to minimum three Gaussian lines of $\pi^* \rightarrow \pi$ transitions (S18 ESI[†]). The 2-quinolylcyanoxime HQCO exhibits ~5 times weaker fluorescence than HBIHCO, HBOCO and HBIMCO, while HBTCO does not appreciably fluoresce under identical conditions. Values of measured emission lifetimes of HBIHCO, HBOCO and HBIMCO in alcohol solutions were in the range 3.4–9.2 ns, which is consistent with the typical fluorescence of conjugated cyclic organic compounds.^{34,56} Deprotonation of the benz-(2-heteroaryl)cyanoximes and formation of the *nitroso*-anions surprisingly decreases the fluorescence intensity by 2 to 6 times.



Fig. 4 Fluorescence spectra of 2.4 mM solutions of 2-(benzheteroaryl)cyanoximes in ethanol at 296 K recorded in a 1 cm cuvette using 400–425 nm excitation.

Complexation reactions. Several other known benz-(2-heteroaryl)cyanoximes form stable coordination compounds with transition metals in solution, and their intensely colored Fe²⁺

and Cu⁺ complexes were found to be useful for analytical applications.⁴⁴ All ligands presented in this paper readily form alkali metal (Na, K, Cs) salts, tetraalkylammonium and tetraphenylphosphonim salts, Ag(I) and Tl(I) complexes.

Characterization of thallium(I) complexes

Only two stoichiometric thallium(I) complexes containing benz-(2-heteroaryl)cyanoximes have been structurally characterized to date: Tl(TLCO)⁴⁵ and Tl(2PCO),⁴⁶ in which planar nitroso anions demonstrate both chelate and bridging binding of metal ions (Scheme 7, binding mode 1). The crystal structure of Tl(I) benz-(2-thiazolyl)cyanoxime complex is completely different from the two compounds published earlier^{45,46} (Scheme 7; binding mode 2).



Structure of TI(BTCO). The molecular structure of this complex represents a centrosymmetric dimer shown in Fig. 5, while bond lengths and valence angles are displayed in Table 2. The BTCO⁻ anion is not planar and has two planes in the molecule: cyanoxime fragment N3-C3-C2-N2-O1 and benzothiazolyl fragment with the value of the dihedral angle between them $\sim 13^{\circ}$. The [Tl(BTCO)]₂ dimeric units connected into a double-stranded onedimensional coordination polymer using the oxime oxygen atoms as the bridge (Fig. 6; Scheme 7, binding mode 2). Individual planar Tl₂O₂ rhombs form a corrugated sheet, two orthogonal projections of which are shown in Fig. 7. It should be noted that there are two slightly different rhombs in the structure: #1 belongs to the dimeric unit [Tl(BTCO)]₂, while #2 represents the junction of dimers into a ladder-type polymer (Fig. 7a,b). The value of the dihedral angle between these rhombs is 107.36°; other geometrical parameters for them are presented in Fig. 7c. Intradimeric Tl-Tl separation in the structure is the shortest: 4.330 Å, while the TI-TI distance inside the one zigzag strand is 4.428 Å (Fig. 7c). These distances are considerably larger than Tl-Tl bonds. All three Tl-O distances in the structure are shorter than the sum of ionic radii for these elements (ca. 2.94 Å from ref. 42, and 2.88 Å from ref. 47,48). The observed double-stranded structural motif of one-dimensional coordination was not expected for



Fig. 5 Molecular structure and numbering scheme in the **[TI(BTCO)**₂] centrosymmetric dimer. H-atoms are omitted for clarity. An ORTEP drawing at 50% thermal ellipsoids probability level.



Fig. 6 One-dimensional polymeric motif in the structure of **Tl(BTCO)**. Hydrogen atoms are omitted for clarity.



Fig. 7 Two orthogonal views of the double stranded polymeric sheet comprised of two different Tl_2O_2 rhombs in the structure of **Tl(BTCO)**. **A** – top view; **B** – side view; **C** – details of geometry of the two adjacent rhombs in the ladder-type structure of **Tl(BTCO)**.

benz-(2-heteroaryl)cyanoximes that are capable of chelate binding of metal ions.^{35,37,49}

Spectroscopic properties of Tl(I) cyanoximates. Tabulated values of the frequencies in the IR spectra of synthesized complexes can be found in S5, S6 ESI[†]. Binding modes of different

cyanoximes established by X-ray analysis in Tl(I) complexes are summarized in Table 5 and were correlated with their IR spectra. Binding modes of benz-(2-heteroaryl)cyanoximes in the reported Tl(I) complexes were deduced using: a) vibrational spectra of labeled (50% ¹⁵N, oxime group) compounds, and b) previously established IR-spectroscopic criteria of coordination of the >C-N=O fragment in metal complexes.⁵⁰ Data suggests binding of cyanoxime ligands to the metal center via the oxygen atom of the oxime-group in Tl(BOCO), Tl(BTCO) and Tl(QCO), leaving nitrogen atoms of the heteroaryl groups not involved in coordination. There are two distinctive bands of v(C=N) and v(N-O) vibrations at *ca* ~1410 and ~1150 cm⁻¹ respectively (S5, S6 ESI[†]). This conclusion was proved in the crystal structure of Tl(BTCO) discussed earlier. The bridging binding mode 2 (Scheme 7) is similar to that reported earlier in structures of thallium(I) arylcyanoximates,²¹ which contain v(C=N) and v(N-O) bands in their IR spectra in the same region. In Tl(BIMCO) and Tl(BIHCO), nitrogen atoms of the heterocyclic fragment are involved in chelation of the metal ion similar to that found in Tl(TLCO)⁴⁵ and Tl(2PCO)⁴⁶ (Table 5 and binding mode 1, Scheme 7). There are multiple bands of the C=N and N-O vibrations in the range of ~1500–1540 cm^{-1} and ~1240–1185 cm^{-1} that are characteristic of both chelate and bridging coordination of the anions to the metal center. We suggest, therefore, that the structures of the former contain five-membered metallocycles, leaving the correctness of such a conclusion to be seen when direct structural information becomes available.

Results of the UV-visible spectroscopic studies of thallium(1) complexes in H₂O and DMSO solutions indicate the presence of anionic ligands and the loss of solid state structure. Thus, the UV-visible and photoluminescence spectra of the TIL in these solvents are identical to those for CsL (L = BTCO⁻, QCO⁻). Values of electrical conductivity of 1 mM solutions of TIL in DMSO were in the range 20–30 mΩ⁻¹ M⁻¹ cm⁻¹ and evidenced in the formation of 1 : 1 electrolytes.⁵¹ The solid state UV-visible absorption spectra of all TIL indicate the presence of an intense broad band of $n \rightarrow \pi^*$ transition similar to that in solution spectra of NBu₄+L⁻ and CsL centered at ~ 430 nm (S21 ESI⁺).

The photoluminescence spectra of solid TlL (as finely ground powders) were recorded at room temperature in the range 300-900 nm using 300, 350, 400 and 450 nm excitation wavelengths (S22 ESI[†]). Regardless of the excitation wavelength, thallium(I) benz-(2-heteroaryl) cyanoximates are blue emitters and show structured bands comprised of multiple, ligand-based transitions centered at ~470 nm (Fig. 8; S23-S25 ESI[†]). Interestingly, solid TIL complexes are luminescent at slightly higher energy (hypsochromic shift ~20 nm) than HL and NaL in solution (S18 ESI[†]). The Tl(BIHCO) is by far the strongest emitter, which is consistent with the brightest photoluminescence of the uncomplexed cyanoxime HBIHCO observed in solution. This superior photoluminescence of 2-benz(imidazolyl) cyanoxime compared to other studied ligands is due to the significant contribution of the resonance form of HBIHCO involving fast prototropic tautomerization. Further investigations of photoluminescence (including low temperature measurements) of this interesting ligand and its metal complexes are warranted for better understanding of properties of compounds and their possible practical applications. Blue emitters are in great demand for new OLED technology (for flat screen display manufacturing)



 Table 5
 Binding modes of the cyanoxime anions in several Tl(1) complexes established by X-ray analysis

 Table 5
 (Contd.)



Commonly used abbreviations for cyanoxime anions (*e.g.* ACO, PiCO, TDCO, *etc.*) correspond to given structural formulas; phen = 1,10-phenanthroline; 18-crown-6 = crown ether; arylcyanoximes = monohalogen substituted α -oximinoacetonitriles.

colors to generate a white luminescent background in these devices.

Concluding remarks

We report a high-yield heterogeneous synthesis of benz-(2heteroaryl)cyanoximes in frozen glacial acetic acid using substituted acetonitriles and solid NaNO₂ as a nitrous acid source. The five cyanoxime ligands obtained were characterized by means of IR, ¹H, ¹³C NMR, UV-visible and fluorescence spectroscopy and X-ray crystallography. Studied benz-(2-heteroaryl) cyanoximes are planar compounds and adopt *trans-anti* (HBIMCO·H₂O) and both *trans-anti* and *cis-anti* (HBOCO) configurations in the solid state. The presence of color and geometrical features of the CNO fragment in the latter compound evidenced its autoionization in the crystal. Three out of five protonated compounds, namely HBI-HCO, HBOCO and HBIMCO, exhibit strong room temperature blue emission centered at ~490 nm with the first compound being the best emitter. All synthesized benz-(2-heteroaryl)cyanoximes easily deprotonate in solution and their anions showed

Chelate or chelate and bridging



since this color is not easily generated in traditionally used materials, but is necessary for blending with the other two principal



Fig. 8 Combined un-normalized room temperature solid state emission spectra of TIL recorded at 400 nm excitation wavelength with emission in the 420–900 nm range. Dotted lines indicate cut-offs of the spectrofluorimeter's second harmonic excitation line (800 nm). An asterisk indicates the instrument's artifact.

pronounced negative solvatochromism of the $n \rightarrow \pi^*$ transitions indicating a substantial degree of charge transfer and its delocalization throughout the anions. The TIL complexes contain bridged and bridged/chelate coordinated cyanoxime anions according to IR spectroscopy and X-ray analysis data. The bridging function of the anion resulted in an unusual (for these ligands) doublestranded ladder type structure of one-dimensional coordination polymer. Tl(1) benz-(2-heteroaryl)cyanoximates demonstrate blue emission in the solid state at room temperature. High intensity fluorescence of HBIHCO and Tl(BIHCO) have warranted their further investigation that will include variable temperature measurements and studies of the efficiency of these systems in OLEDs.

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